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**SOLID CATALYST COMPONENT FOR POLYMERIZATION AND  
COPOLYMERIZATION OF ETHYLENE, AND, PROCESS FOR OBTAINING  
THE SAME**

- 5       The present invention relates to a solid catalyst component for ethylene polymerization and copolymerization, composed of a carrier of particulate silica and a catalytically active portion including titanium, magnesium, chlorine, alkoxy groups and at least one organometallic compound of the groups 1, 2, 12 or 13 of the periodic table. The process for obtaining the catalyst of the present
- 10      invention comprises the steps of:
- (a) impregnating an activated silica in particles using a solution of an organometallic compound of the groups 1, 2, 12 or 13 of the periodic table, in an inert organic solvent;
  - (b) removing the supernatant liquid from the step (a);
  - 15      (c) preparing a solution obtained by reacting at least one magnesium compound, selected from magnesium halides and magnesium alkoxides and at least one titanium compound selected from titanium alkoxides and titanium halogen alkoxides;
  - (d) impregnating the silica obtained on (b) using the solution prepared in

20      (c);

  - (e) optionally reacting the solid obtained in (d) with a reducing agent;
  - (f) reacting the solid obtained in (d) or (e) with a halogenating agent;
  - (g) treating thermally the solid obtained in (f);
  - (h) washing the solid obtained in (g) with an inert organic solvent;

25      (i) optionally, washing the solid obtained in (h) with a solution of one or more organometallic compounds of the groups 1, 2, 12 or 13 of the periodic table.

The catalyst component obtained is especially suitable for the production of homo- and copolymers of ethylene as narrow molecular weight distribution

30      high density polyethylene and linear low density polyethylene with controlled morphology and improved structure.

polyethylene with 0.919 g/ml of polymer density has a xylene soluble content of 12.5% by weight.

### SUMMARY OF THE INVENTION

The present invention relates to a solid catalyst component for ethylene 5 polymerization and copolymerization, composed of a carrier of particulate silica and a catalytically active portion including titanium, magnesium, chlorine, alkoxy groups and at least one organometallic compound of the groups 1, 2, 12 or 13 of the periodic table. The process for obtaining the catalyst of the present invention comprises the steps of:

- 10 (a) impregnating an activated silica in particles using a solution of an organometallic compound of the groups 1, 2, 12 or 13 of the periodic table, in an inert organic solvent;
- (b) removing the supernatant liquid from the step (a);
- (c) preparing a solution obtained by reacting at least one magnesium 15 compound, selected from magnesium halides and magnesium alkoxides and at least one titanium compound selected from titanium alkoxides and titanium halogen alkoxides;
- (d) impregnating the silica obtained on (b) using the solution prepared in (c);
- 20 (e) optionally reacting the solid obtained in (d) with a reducing agent;
- (f) reacting the solid obtained in (d) or (e) with a halogenating agent;
- (g) treating thermally the solid obtained in (f);
- (h) washing the solid obtained in (g) with an inert organic solvent;
- (i) optionally, washing the solid obtained in (h) with a solution of one or 25 more metal-alkyl halide compounds of the groups 1, 2, 12 or 13 of the periodic table.

Therefore, the present invention provides a catalyst especially suitable for the production of ethylene homo- and copolymers as narrow molecular weight distribution high density polyethylene (NMWHDPE) and linear low 30 density polyethylene (LLDPE) with controlled morphology and improved structure.

In step (a) of the process according to the present invention, the preferable silica for this purpose is a microspheroidal, porous silica having an average particle size ranging from 10 to 120  $\mu\text{m}$ , preferably between 15 and 100  $\mu\text{m}$ , a  $\text{SiO}_2$  contents of > 90% by weight, a surface area ranging from 250 to 500  $\text{m}^2/\text{g}$ , preferably between 300 and 400  $\text{m}^2/\text{g}$ , a pore volume ranging from 1.0 to 2.0  $\text{ml/g}$ , preferably between 1.5 and 1.8  $\text{ml/g}$ , and an average pore diameter ranging from 10 to 40 nm, preferably between 20 and 30 nm. This silica should be submitted to an activation treatment before being impregnated, which can be carried out by heating the silica in an inert atmosphere, at a temperature ranging from 100 to 750°C, over a period from 1 to 20 hours. The amount of remained OH on silica surface after this treatment ranges from 0.1 to 2 mmoles OH per g of silica, preferably between 0.5 and 1.5 mmoles OH per g of silica.

The impregnation is preferably carried out by suspending 10 to 20 parts by weight of silica for each 100 parts by volume of solution of organometallic compound of the groups 1, 2, 12 or 13, in aliphatic hydrocarbons, and maintained under stirring at a temperature which ranges from room temperature to the boiling point of the solution of organometallic compound of the groups 1, 2, 12 or 13, in aliphatic hydrocarbons, preferably at room temperature, over a period from 30 to 120 minutes, preferably between 50 and 60 minutes.

The organometallic compounds of groups 1, 2, 12 or 13 of the periodic table suitable for use in the step (a) are alkyl compounds and alkyl halide compounds of metals belonging to these groups, and preferably aluminum, magnesium, lithium and zinc compounds. Specific examples of these compounds are trimethylaluminum, triethylaluminum (TEAL), methylaluminum dichloride, methylaluminum sesquichloride, isobutylaluminum dichloride, isobutylaluminum sesquichloride, ethylaluminum dichloride (EADC), diethylaluminum chloride (DEAC), ethylaluminum sesquichloride (EASC), tri-n-hexylaluminum (Tn-HAL), tri-n-octylaluminum (TnOAL), butyl ethylmagnesium (BEM), butyl octylmagnesium (BOMAG), methylmagnesium chloride and ethylmagnesium chloride. They can be used concentrated or preferably

parts by weight of silica, obtained on step (b), for each 5 to 200 parts by volume of the component prepared on step (c) and after dilution in the inert organic solvent. The suspension is maintained under stirring at a temperature that ranges from room temperature to the boiling point of the mixture, preferably at 5 60°C, over a period of time from 30 to 180 minutes, preferably between 50 and 60 minutes. In this way a solid component suspended in an inert organic solvent is obtained.

Optionally the solid component obtained in step (d) can be submitted to reducing conditions in a step (e). Said result is obtained, for example, by using 10 reducing agents, such as Na-alkyls, Li-alkyls, Zn-alkyls, Mg-alkyls and corresponding aryl-derivatives, Grignard compounds of the type RMgX, wherein R represents a linear or branched alkyl group, containing from 1 to 10 carbons or aryl-derivatives and X represents a halogen atom and preferably a chlorine atom, Al-alkyl halide compounds or by using reducing agents such as silicon 15 compounds. Particularly effective silicone compounds are the polymethylhydrosiloxanes in which the monomer unit has the general formula [-HSiR-O-]<sub>n</sub> wherein R is H, halogen, alkyl with 1 to 10 carbon atoms, aryl with 6 to 10 carbon atoms, alkoxy with 1 to 10 carbon atoms, aryloxy with 6 to 10 carbon atoms or carboxyl with 1 to 10 carbon atoms, and n is a degree of 20 polymerization that ranges between 5 and 100. Specific examples of such polymethylhydrosiloxanes (PMHS) include the compounds: (CH<sub>3</sub>)<sub>3</sub>SiO[(CH<sub>3</sub>)HSiO]<sub>n</sub>Si(CH<sub>3</sub>)<sub>3</sub>, (CH<sub>3</sub>HSiO)<sub>4</sub>, (CH<sub>3</sub>HSiO)<sub>3</sub>, H<sub>3</sub>Si-O-SiH<sub>2</sub>-OSiH<sub>3</sub>, phenylhydropolysiloxanes in which the hydrogen atoms can be partially replaced by methyl groups.

25 Other silicon compounds useful as reducing agents in the practice of this invention are: silanes (Si<sub>m</sub>H<sub>2m+2</sub>, in which m is a number equal to or higher than 1), alkyl-silanes or aryl-silanes (R<sub>x</sub>SiH<sub>4-x</sub>, in which R is alkyl or aryl and x is a number varying from 1 to 3) and alkoxy-silanes or aryloxy-silanes (RO<sub>x</sub>SiH<sub>4-x</sub>, in which R is alkyl or aryl and x is a number varying from 1 to 3).

30 The reducing agent chosen from the above examples, preferably polymethylhydrosiloxanes (PMHS), is added to the solid obtained in the step

carbon atoms, having a content of units derived from ethylene greater than approximately 80% by weight. These products have an improved structure due to the very good comonomer insertion and, in most cases, they have also a narrow molecular weight distribution ( $MFR < 27$ ). Hence the low xylene soluble 5 contents are obtained, allowing the production of films with superior optical properties and very low blocking. The LMDPE products are particularly useful for rotomolding applications;

- Elastomeric copolymers of ethylene and propylene and elastomeric terpolymers of ethylene and propylene with minor amounts of a diene, having a 10 content of units derived from ethylene comprised between about 30 and 70% by weight.

### EXAMPLES

The present invention is now explained in more details by means of the following Examples, which should not be understood as limiting the scope of 15 the invention.

The properties here indicated are determined according to the following methods:

- Surface area and pore volume: determined by nitrogen adsorption according to the B.E.T methodology using a "Micromeritics ASAP 2010" apparatus.
- Size of the catalyst particles: determined according to a method based on the principle of optical diffraction of monochromatic laser light, using the "Malvern Instr. 2600" apparatus.
- MIE melt index: ASTM D-1238, condition E
- MIF melt index: ASTM D-1238, condition F
- MFR melt flow ratio: MIF/MIE
- Flowability: it is the time required by 100 g of polymer to flow through a stainless steel funnel (outlet opening diameter of 12.7 mm and side walls at  $20^\circ$  to the vertical).
- Bulk density: ASTM D-1895

CLAIMS

1. A process for obtaining a solid catalyst component for ethylene polymerization and copolymerization, wherein a carrier of particulate silica is impregnated with a catalytically active portion including titanium, magnesium, chlorine, alkoxy groups and at least one organometallic compound of the groups 1, 2, 12 or 13 of the periodic table, the process comprising the steps of:
  - (a) impregnating an activated particulate silica in particles using a solution of an organometallic compound of the groups 1, 2, 12 or 13 of the periodic table, in an inert organic solvent;
  - (b) removing the supernatant liquid from the step (a);
  - (c) preparing a solution obtained by reacting at least one magnesium compound, selected from magnesium halides and magnesium alkoxides and at least one titanium compound selected from titanium alkoxides and titanium halogen alkoxides;
  - (d) impregnating the silica obtained on (b) using the solution prepared in (c);
  - (e) optionally reacting the solid obtained in (d) with a reducing agent;
  - (f) reacting the solid obtained in (d) or (e) with a halogenating agent;
  - (g) treating thermally the solid obtained in (f);
  - (h) washing the solid obtained in (g) with an inert organic solvent;
  - (i) optionally washing the solid obtained in (h) with a solution of one or more organometallic compounds of the groups 1, 2, 12 or 13 of the periodic table.
2. A process for obtaining a solid catalyst component according to claim 1, wherein the activated particulate silica used in step (a) is a microspheroidal, porous silica.
3. A process for obtaining a solid catalyst component according to claim 1 or 2, wherein the activated particulate silica used in step (a) has an average particle size ranging from 10 to 120 µm.
4. A process for obtaining a solid catalyst component according to any one of claims 1 to 3, wherein the activated particulate silica used in step (a) has a surface area ranging from 250 to 500 m<sup>2</sup>/g.

5. A process for obtaining a solid catalyst component according to claims 1 to 3, wherein the activated particulate silica used in step (a) has a pore volume ranging from 1.0 to 2.0 ml/g.
6. A process for obtaining a solid catalyst component according to claim 1,  
5 wherein the organometallic compounds of groups 1, 2, 12 or 13 of the periodic table used in step (a) is trimethylaluminum, triethylaluminum (TEAL), methylaluminum dichloride, methylaluminum sesquichloride, isobutylaluminum dichloride, isobutylaluminum sesquichloride, ethylaluminum dichloride (EADC), diethylaluminum chloride (DEAC),  
10 ethylaluminum sesquichloride (EASC), tri-n-hexylaluminum (Tn-HAL), tri-n-octylaluminum (TnOAL), butyl ethylmagnesium (BEM), butyl octylmagnesium (BOMAG), methylmagnesium chloride or ethylmagnesium chloride.
7. A process for obtaining a solid catalyst component according to claim 1,  
15 wherein the magnesium compound used to prepare the solution of the step (c) is magnesium dichloride, magnesium diethylate, magnesium di-n-butylate, magnesium diisopropylate or magnesium diisobutylate.
8. A process for obtaining a solid catalyst component according to claim 1 or 7,  
20 wherein the magnesium compound used to prepare the solution of the step (c) is used in an amount ranging from 0.0024 to 0.24 g of magnesium per g of silica.
9. A process for obtaining a solid catalyst component according to claim 1,  
25 wherein the titanium compound used to prepare the solution of the step (c) is titanium tetra-n-propylate, titanium tetra-n-butyrate, titanium tetra-i-propylate, titanium tetra-i-butyrate or the corresponding titanium mono- or di-chloroalkoxides.
10. A process for obtaining a solid catalyst component according to claim 1 or 9,  
wherein the titanium compound used to prepare the solution of the step (c)  
is used in an amount ranging from 0.01 to 1 g of titanium per g of silica.
- 30 11. A process for obtaining a solid catalyst component according to any one of claims 1, 7, 8, 9 or 10, wherein the molar ratio Ti/Mg used to prepare the solution of the step (c) is comprised between 0.3 and 4.

12. A process for obtaining a solid catalyst component according to claim 1, wherein the reducing agent used in the step (e) is Na-alkyl, Li-alkyl, Zn-alkyl, Mg-alkyl and corresponding aryl-derivatives, Grignard compounds of the type RMgX or polyhydrosiloxanes.
- 5 13. A process for obtaining a solid catalyst component according to claim 1 or 12, wherein the reducing agent used in the step (e) is  $(CH_3)_3SiO[(CH_3)HSiO]_nSi(CH_3)_3$ ,  $(CH_3HSiO)_4$ ,  $(CH_3HSiO)_3$ ,  $H_3Si-O-SiH_2-OSiH_3$  or phenylhydropolysiloxanes in which the hydrogen atoms can be partially replaced by methyl groups.
- 10 14. A process for obtaining a solid catalyst component according to claim 1 or 12, wherein the reducing agent used in the step (e) is used in an amount ranging from 0 to 2 moles per mole of titanium.
- 15 15. A process for obtaining a solid catalyst component according to claim 1, wherein the halogenating agent used in the step (f) is methylaluminum dichloride, methylaluminum sesquichloride, isobutylaluminum dichloride, isobutylaluminum sesquichloride, ethylaluminum dichloride (EADC), diethylaluminum chloride (DEAC), ethylaluminum sesquichloride (EASC),  $SiCl_4$ ,  $SnCl_4$ ,  $HCl$ ,  $Cl_2$ ,  $HSiCl_3$ , aluminum chloride, ethylboron dichloride, boron chloride, diethylboron chloride,  $HCCl_3$ ,  $PCl_3$ ,  $POCl_3$ , acetyl chlorides,
- 20 thionyl chloride, sulfur chloride, methyl trichlorosilane, dimethyl dichlorosilane,  $TiCl_4$ ,  $VCl_4$ ,  $CCl_4$ , t-butyl chloride, n-butyl chloride, chloroform, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,2-dichloroethane or dichloromethane.
- 25 16. A process for obtaining a solid catalyst component according to claim 1 or 15, wherein the halogenating agent used in the step (f) is used in an amount ranging from 0.5 to 3 moles of halogenating agent per mole of titanium.
17. A process for obtaining a solid catalyst component according to claim 1, wherein the thermal treatment of the step (g) is conducted from 0.5 hour to 5 hours and at a temperature from 60°C to 120°C.
- 30 18. A process for obtaining a solid catalyst component according to claim 1, wherein two different organometallic compounds are used in the step (i) to wash the solid obtained in step (h).

19. A process for obtaining a solid catalyst component according to claim 1 or 18, wherein the two different organometallic compounds in the step (i) are fed together, mixed in the same solution.
20. A process for obtaining a solid catalyst component according to claim 1 or 5 18, wherein the two different organometallic compounds in the step (i) are fed together, in individual solutions.
21. A process for obtaining a solid catalyst component according to claim 1 or 18, wherein the two different organometallic compounds in the step (i) are fed one after the other, in individual solutions.
- 10 22. A process for obtaining a solid catalyst component according to claims 1, 18, 19, 20 or 21 wherein the organometallic compound used in the step (i) is methylaluminum dichloride, methylaluminum sesquichloride, isobutylaluminum dichloride, isobutylaluminum sesquichloride, ethylaluminum dichloride (EADC), diethylaluminum chloride (DEAC), 15 ethylaluminum sesquichloride (EASC), tri-n-hexylaluminum (Tn-HAL) or tri-n-octylaluminum (TnOAL).
23. A process for obtaining a solid catalyst component according to claim 1, wherein the inert organic solvent used is hexane, heptane, octane or isoparaffin.
- 20 24. A solid catalyst component for ethylene polymerization and copolymerization, obtained according to the process described in claim 1, comprising a carrier of particulate silica and a catalytically active portion including titanium, magnesium, chlorine, alkoxy groups and at least one organometallic compound of the groups 1, 2, 12 or 13 of the periodic table.
- 25 25. A solid catalyst component according to claim 24, wherein the solid catalyst component morphology is spheroidal.
26. A solid catalyst component according to claim 24, wherein the solid catalyst has an average particle size ranging from 10 to 120 µm.
27. A solid catalyst component according to claim 24, wherein the solid catalyst 30 has a surface area ranging from 80 to 300 m<sup>2</sup>/g.
28. A solid catalyst component according to claim 24, wherein the solid catalyst has a pore volume ranging from 0.1 to 1.0 ml/g.

- 29.A solid catalyst component according to claim 24, wherein the magnesium is present in an amount ranging from 0.003 to 0.03 g of magnesium per g of solid catalyst.
- 30.A solid catalyst component according to claim 24, wherein the titanium is present in an amount ranging from 0.005 to 0.02 g of titanium per g of solid catalyst.
- 5 31.A solid catalyst component according to claim 24, wherein the organometallic compound of the groups 1, 2, 12 or 13 of the periodic table is present in an amount ranging from 0.003 to 0.03 g of metal per g of solid catalyst.
- 10 32.A solid catalyst component according to claim 24 or 31, wherein the organometallic compound of the groups 1, 2, 12 or 13 of the periodic table is an organo-aluminum, an organo-magnesium, an organo-lithium or an organo-zinc compound.
- 15 33.A solid catalyst component according to claim 24, wherein the alkoxy groups is present in an amount ranging from 0.03 to 0.08 g of alkoxy groups per g of solid catalyst.
- 34.A solid catalyst component according to claim 24 or 33, wherein the alkoxy groups is n-propoxy, i-propoxy, n-butoxy or i-butoxy.
- 20 35.A solid catalyst component according to claim 24, wherein the chlorine is present in an amount ranging from 0.05 to 0.12 g of chlorine atoms per g of solid catalyst.
- 36.A process for ethylene polymerization and copolymerization wherein is used the catalyst according to one or more of the claims 24 to 35.
- 25 37.A process for ethylene polymerization and copolymerization according to claim 36, wherein it is carried out in gas phase.
- 38.Process for ethylene polymerization and copolymerization according to claim 36 wherein the co-catalyst used in the polymerization process is an alkyl aluminum.
- 30 39.Process for ethylene polymerization and copolymerization according to claims 36 or 38 wherein the co-catalyst used in the polymerization process is trimethyl aluminum or triethyl aluminum.

40. Process for ethylene polymerization and copolymerization according to claims 36, 38 or 39 wherein mass ratio co-catalyst:catalyst in the polymerization process is between 0.5:1 and 6:1.
41. A process for ethylene polymerization and copolymerization according to 5 claims 36, 37 or 38, wherein the catalyst is fed in dry bulk powder, in paste, in oil suspension or in solvent suspension.
42. A process for ethylene polymerization and copolymerization according to claims 36 or 41, wherein the catalyst is fed directly into the polymerization reactor.
- 10 43. A process for ethylene polymerization and copolymerization according to claims 36 or 41, wherein the catalyst is prepolymerized before to be fed into the polymerization reactor.
44. A process for ethylene polymerization and copolymerization according to 15 claims 36, 41 or 43, wherein the catalyst is prepolymerized with ethylene or propylene before to be fed into the polymerization reactor.
45. A linear low density polyethylene produced according to the process of the claims 36 to 44.
46. A linear medium density polyethylene produced according to the process of the claims 36 to 44.
- 20 47. A high density polyethylene produced according to the process of the claims 36 to 44.